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(54) Name of the invention: Thermoplastic Resin Composition

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(Note: Names, addresses, company names and brand names are translated in the most common manner. Japanese language does not have singular or plural words unless otherwise specified by a numeral prefix or a general form of plurality suffix.)

(54) [Name of the Invention]

Thermoplastic Resin Composition

(57) [Abstract]

The present invention is an invention about a light weight thermoplastic resin composition material that has excellent mechanical strength, that has an olefin type polymer material and a crosslinked styrene type polymer material as main components.

[Structure]

Thermoplastic resin composition material characterized by the fact it is comprised of (i) olefin type polymer material, (ro) crosslinked styrene type polymer material that has a density in the range of 0.5 ~ 1.1, and (ha) a hydrogenated block copolymer material that is formed from (A) at least one type of block segment that is selected from (A-1) a styrene type polymer material block segment or (A-2) polybutadiene block segment, that contains no more than 20 % or less of 1, 2 – vinyl bond content, and together with that it is formed from (B) a butadiene type (co) polymer material block segment and/or isoprene type (co) polymer material block segment, which contain at least 20 % or more of 1, 2- vinyl bond content and where the block structure is either a linear type or a branched type structure, and where the amount of the unsaturated double bonds of the block copolymer material is at least 90 % or higher.

[Scope of the Claims of the Invention]

[Claim 1]

Thermoplastic resin composition material characterized by the fact it is comprised of

(i) olefin type polymer material,

(ro) crosslinked styrene type polymer material that has a density in the range of 0.5 ~ 1.1, and

(ha) a hydrogenated block copolymer material that is formed from (A) at least one type of block segment that is selected from (A-1) a styrene type polymer material block segment or (A-2) polybutadiene block segment, that contains no more than 20 % or less of 1, 2 – vinyl bond content, and together with that it is formed from (B) a butadiene type (co) polymer material block segment and/or isoprene type (co) polymer material block segment, which contain at least 20 % or more of 1, 2- vinyl bond content and where the block structure is either a linear type or a branched type structure, and where the amount of the unsaturated double bonds of the block copolymer material is at least 90 % or higher.

[Detailed Description of the Invention]

[0001]

[Technological Sphere Pertaining to the Invention]

The present invention is an invention about a light weight thermoplastic resin composition material that has excellent mechanical strength, that has an olefin type polymer material and a crosslinked styrene type polymer material as main components.

[0002]

[Prior Art]

The polyolefin type polymer material is inexpensive and it is the resin material that is produced and consumed in maximum amounts. Also, because of the fact that it is a material that has excellent molding processing properties, it is widely used as different types of molded materials. On the other hand, the achievement of light weight resins has attracted a lot of attention in the automobile industry sphere, and in the case of the use of these resin materials in the automobile industry, from the point of view of designing an improvement of the automobile fuel consumption and performance, achieving light weight for the automobile, has become a significant technological problem. Also, besides that in other technological spheres, like also in the home electrical sphere etc., the issue where by making the resin material be light weight, the transport becomes easy, resources are eliminated, the amount of the waste plastic materials, is reduced, etc., has become a technological problem. In the past, as a method for making the resin material be light weight, different methods have been devised, for example, there has been the method where the achievement of light weight has been accomplished by the introduction of crosslinked polymer particles in a thermoplastic resin material (Japanese Patent Application Laid-Open Number Hei-Sei 4-12677121). However, according to this method, even though it is possible to achieve a light weight, because of the fact that the resin material and the crosslinked styrene type polymer material, are mutually incompatible, there is the danger that a phase separation would occur in the simple mixed material, and it has not been a material that can withstand a practical application because of the mechanical strength of the resin material. It has been known that usually, in order to improve the compatibility properties of a mixture material containing two types of materials, a compatibilizer can be used. However, compatibilizers that are appropriate for compatibilizing an olefin type polymer material and a crosslinked styrene type polymer material, have not been known.

[0003]

The present invention is an invention that has made the problems of the above described technological sphere be its background, and it is an invention that has as a goal to obtain a thermoplastic resin composition material that is light weight and that also has excellent mechanical strength by adding a hydrogenated block copolymer material with a specific molecular design, as a compatibilization improvement agent, to a polymer

mixed material comprised of an olefin type polymer material and a crosslinked styrene type polymer material.

[0004]

[Measures to Solve the Problems]

The present invention is an invention that is suggesting a thermoplastic resin composition material characterized by the fact it is comprised of (i) olefin type polymer material, (ro) crosslinked styrene type polymer material that has a density in the range of 0.5 ~ 1.1, and (ha) a hydrogenated block copolymer material that is formed from (A) at least one type of block segment that is selected from (A-1) a styrene type polymer material block segment or (A-2) polybutadiene block segment, that contains no more than 20 % or less of 1, 2 – vinyl bond content, and together with that it is formed from (B) a butadiene type (co) polymer material block segment and/or isoprene type (co) polymer material block segment, which contain at least 20 % or more of 1, 2- vinyl bond content and where the block structure is either a linear type or a branched type structure, and where the amount of the unsaturated double bonds of the block copolymer material is at least 90 % or higher.

[0005]

According to the present invention, as the olefin type polymer material, which forms the structure of the component (i), a polymer material is used that uses as its main monomer component an α-mono olefin, that has a number of carbon atoms that is in the range of 2 ~ 8. As detailed examples of this olefin type polymer material, there are the following materials: low density polyethylene, high density polyethylene, linear type low density polyethylene, polypropylene, ethylene – propylene random copolymer material, ethylene – propylene block copolymer material, polymethyl pentene, polybutene – 1, etc. And these materials can be used individually as one single type of material, or they can be used as mixtures of 2 and more types of materials. Especially preferred olefin type polymer materials are the polymer materials that have ethylene or propylene as their main monomer components, and in more details, they are different types of polyethylene, polypropylene, ethylene – vinyl acetate random copolymers, ethylene – (meth)acrylic acid random copolymers, ethylene – glycidyl methacrylate random copolymer materials, etc., ethylene type random copolymer

materials, propylene type random or propylene type block copolymer materials, and then also mixtures thereof.

[0006]

According to the present invention, the crosslinked styrene type polymer material that forms the structure of the component (ro), can be (co) polymer materials that have as their main components styrene, p-methyl styrene, α-methyl styrene, etc., styrene type monomers and divinyl benzene, polyvalent alcohol etc., di or tri- (meth)acrylic acid esters (ethylene glycol diacrylate, ethylene glycol dimethacrylate) etc., polyfunctional monomers. In these crosslinked styrene type polymer materials, besides the styrene type monomer material and the polyfunctional monomer material, it is also a good option if then also acrylonitrile, methyl methacrylate, maleic acid anhydride, etc., are also copolymerized. According to the present invention, the crosslinked styrene type polymer material can be used as a water dispersion material, or it can be used as a powder material obtained after the drying. The powder material obtained after the drying is preferred from operational properties point of view. Regarding the drying, spray-dry drying etc., different methods can be used, however, preferably, the spray0-dry method is used. According to the present invention the density of the crosslinked styrene type polymer material is in the range of 0.5 ~ 1.1, and preferably it is in the range of 0.6 ~ 0.9, and when the density of the crosslinked styrene type polymer material is decreased, it is preferred because the crosslinked styrene type polymer material is then a hollow or highly porous type particle material.

There are no particular limitations regarding the manufacturing method for the preparation of the crosslinked hollow particles, however, these can be appropriately manufactured according to the methods that have been reported in the descriptions of the Japanese Patent Application Laid-Open Number Showa 62-127336, Japanese patent Application Laid Open Number Showa 61-185505.

[0007]

Then, the particle diameter in the case when particles of the crosslinked styrene type polymer material, are used, is usually in the range of 0.1 ~ 10 microns. According to the present invention, the preferred polymer compositions of the hollow or multiporous crosslinked styrene particles are

methyl methacrylate/Divinylbenzene/methacrylic acid, methyl methacrylate/divinyl benzene/styrene and or α-methyl styrene/methacrylic acid, styrene and or α-methyl styrene/divinyl benzene/methacrylic acid, etc.

[0008]

Regarding the component (ha) according to the present invention, it is a hydrogenated block copolymer material that is formed from (A), which is at least one type of block segment that is selected from (A-1) a styrene type polymer material block segment (here below it is called "block A1"), or (A-2) polybutadiene block segment, that contains no more than 20 % or less of 1, 2 – vinyl bond content (here below called "block A2"), and that is contained in an amount that is in the range of 2 ~ 98 weight %; and together with that it is formed from 20 ~ 95 % of the component (B) (here below called "Block B"), which is comprised of 50 ~ 100 weight % of butadiene and/or isoprene type and 50 ~ 0 weight % of another monomer material, where this component (B) is formed from a butadiene (co) polymer block segment, where the contained amount of the 1, 2-vinyl bond in the butadiene part is in the range of 20 ~ 95 %, and/or an isoprene (co) polymer material block segment where the contained amount of the 1, 2 – vinyl bond in the isoprene part is in the range of 20 ~ 95 %; and together with that it is formed so that [(A) + (B) = 100 weight %], and also, it is hydrogenated so that the unsaturated double bond of the block copolymer material whose block structure is a linear type or a branched type structure, is at least 90 % or higher.

[0009]

Preferred detailed design principles for the block A and block B are summarized in the below described.

Case 1 (Case where the olefin type polymer material is a material that uses ethylene as its main monomer component):

When the block A2 in the (ha) component is formed so that its structure is made to resemble that of polyolefin etc., through hydrogenation, its compatibility properties relative to the olefin type polymer material (for example: polyethylene), which has ethylene as its main component, are excellent. Consequently, a material that contains the block A2 is especially preferred as a compatibilizer agent for the component (i),

which uses as its component the olefin type polymer material, that has ethylene as its main monomer component. In this case, it is preferred to design as the block B a segment that has excellent rubber properties, because the friction (wear) resistant properties are significantly increased. In the case when the block B is designed as a segment that has excellent rubber properties, it is preferred that the content of the vinyl bond of the diene part in the block B, has an appropriate value that is within the range reported according to the claims of the invention. For example, the content of the vinyl bond of the diene part in the block B, in the case of butadiene is in the range of 30 ~ 55 weight %, and preferably, it is in the range of 35 ~ 50 weight %, and in the case of isoprene, it is in no more than 40 weight % or less, and preferably, it is no more than 30 weight % or less. By having such vinyl bond content that is within this range, the block B shows excellent rubber properties.

[0010]

Case 2 (Case when the olefin type polymer material has as its main monomer material component a monomer material other than ethylene): In the case when the olefin type polymer material, that forms the structure of the component (i), has as its main monomer material component a monomer material other than ethylene, it is preferred that the block B, which forms the structure of the component (ha) has a molecular design so that the material has excellent compatibility properties relative to olefin type polymer material. In this case, it is preferred that the content of the vinyl bond of the diene part in the block B, has an appropriate value that is within the range reported according to the claims of the invention. In order to obtain especially excellent compatibility properties of the block B relative to the olefin type polymer material, it is especially preferred that the vinyl bond content in the above block B is made to be as a high as possible. Namely, the content of the vinyl bond of the diene part in the block B, in the case of butadiene is preferred to be in the range of 65 ~ 95 weight %, and especially preferably, it is in the range of 70 ~ 90 weight %, and in the case of isoprene, it is preferred to be in the range of 50 ~ 95 weight %, and especially preferably, it is in the range of 55 ~ 90 weight %. In the case of this Case 2, it is a good option if the block A2 of the component (ha) is present, and it is also a good option it is not present, however, in the case of a block B, that has been designed so that it has a high vinyl bond content, there is the trend that it is easy to stick and its handling

properties become poor. Together with decreasing the amount of the block A2, the sticking properties are appropriate and the handling properties become good, and that is a preferred option.

[0011]

After that the structures of each the block A1, block A2 and block B, that form the structure of the component (ha), will be explained. The styrene type monomer material that is used in block A1, is styrene, α–methyl styrene, p-methyl styrene, etc., aromatic vinyl compounds, and these can be used individually, or they can be used as a mixture. The weight average molecular weight of the block A1, usually, is in the range of 5,000 ~ 200,000, and preferably it is in the range of 10,000 ~ 150,000, and then more preferably, it is in the range of 15,000 ~ 100,000. In the case when that weight average molecular weight is less than 5,000, the compatibility properties relative to the crosslinked styrene type polymer material, that forms the structure of the component (ro), are poor, and because of that, it is not a preferred option. And on the other hand, in the case when the weight average molecular weight exceeds 200,000, the flowability properties become poor, and the processing properties are deteriorated, and that is why it is not preferred. The proportion of the block A1 in the component (ha), is in the range of 2 ~ 98 weight %, and preferably, it is in the range of 10 ~ 80 weight %, and then more preferably, it is in the range of 15 ~ 70 weight %. And in the case when that proportion is less than 2 weight %, or when it exceeds 98 weight %, the capability as a compatibilizing agent is poor.

[0012]

Regarding the block B, it is formed from in the range of 50 ~ 100 weight % of butadiene and/or isoprene, and in the range of 50 ~ 0 weight % of another type of monomer material, and it is a butadiene (co) polymer material block segment, where the content of the 1, 2 – vinyl bond in the butadiene part is in the range of 20 ~ 95 %, and /or, an isoprene (co) polymer material block segment, where the content of the vinyl bond in the isoprene part, is in the range of 10 ~ 95 %. The fact that the block B is a block segment that significantly varies with the role that must be fulfilled depending on the target application of the structure of the whole body of the component (ro), is according to the described here below. Moreover, according to the present invention, the 1, 2- vinyl bond content of the butadiene part is represented by the amount of butadiene

containing an 1, 2 – vinyl bond that is found in the butadiene block, and the contained amount of the vinyl bond in the isoprene part, is represented by the total amount of the isoprene containing a 1, 2 – vinyl bond, and isoprene containing 3, 4 – bond, that are found in the isoprene block.

[0013]

Then, as the other monomer material that is used in the block B, it is possible to use styrene, α-methyl styrene, p-methyl styrene, etc., aromatic vinyl compounds, methyl methacrylate, methyl acrylate etc., esters of the (meth)acrylic acid, 2, 3 – dimethyl – 1, 3 – butadiene, 1, 3 – pentadiene, 2 – methyl – 1, 3 – pentadiene, 1, 3 – hexadiene, 4, 5 – diethyl – 1, 3 – octadiene, 3 – butyl – 1, 3 – octadiene, chloroprene, etc., conjugated dienes, etc., however, styrene is especially preferred. The used amount of this other monomer material is in the range of 0 ~ 50 weight %, preferably, it is in the range of 0 ~ 40 weight %, and more preferably, it is in the range of 0 ~ 30 weight % of the total amount of material that forms the structure of the Block B. In the case when as the other monomer material, styrene etc., monomer material, that leads to the obtaining of a rigid homopolymer type material, is used, if the amount that is used exceeds 50 weight %, the glass transition point temperature of the block B after the hydrogenation is increased, and the performance as an elastomer type material, is decreased (in the case of medium ~ low vinyl content), or because of the decrease of the conjugated diene component amount inside the block B, the compatibility properties relative to the olefin type polymer material, that forms the structure of the component (i), are decreased (high vinyl content case), and because of that, neither of these options are preferred.

[0014]

Regarding the vinyl bond content of the block B, in the case when the above block B is a butadiene (co) polymer material, it is in the range of 20 ~ 95 weight %, and preferably, it is in the range of 20 ~ 90 weight %, and in the case when it is an isoprene (co) polymer material, it is in the range of 10 ~ 95 weight %, and preferably it is in the range of 15 ~ 90 weight %. In the case when the contained amount of vinyl bond in the block B is lower than the lower limit, or it exceeds the higher limit, after the hydrogenation, the corresponding polyethylene chain, demonstrates a

crystalline structure due to the polybutene – 1 chain, and the capability as the (ha) component elastomer are poor, and because of that, these are not preferred options. Moreover, regarding the weight average molecular weight of the block B, usually, it is in the range of 5,000 ~ 250,000, and preferably, it is in the range of 10,000 ~ 200,000, and then more preferably, it is in the range of 15,000 ~ 150,000. In the case when that weight average molecular weight is less than 5,000, the effect of improvement of the friction (wear) resistant properties, is poor, and also, the compatibility properties relative to the olefin type polymer material, that forms the structure of the component (I)< are poor, and because of that it is not a preferred option. And on the other hand, in the case when that weight average molecular weight exceeds 250,000, the flowability properties are poor, and the processing properties and molding properties are deteriorated, and because of that it is not a preferred option. Regarding the proportion of the block B, it is in the range of 2 ~ 98 weight % in the component (ha), and preferably, it is in the range of 10 ~ 80 weight %, and then more preferably, it is in the range of 15 ~ 70 weight %. And in the case when the amount is less than 2 weight %, or in the case when the amount exceeds 98 weight %, the performance as a component (ha) compatibilizing agent, is decreased, and that is why these are not preferred options.

[0015]

Then, regarding the block A2 that forms the structure of the component (ha), through hydrogenation, it becomes a block segment of a structure that resembles that of crystalline polyethylene, and especially, it has excellent compatibility properties relative to olefin type polymer material, that have ethylene as their main component. Regarding the 1, 2 vinyl bond content of the block A2, it is the main factor for controlling the crystalline properties of the block A2 after the hydrogenation, and it is no more than 15 weight % or less, of the component (ha). In the case when this 1, 2 – vinyl bond content exceeds 15 weight %, the crystallinity properties of the ethylene chain, are decreased and because of that the compatibility properties relative to the olefin type polymer material, that has ethylene as its main component, are decreased. Moreover, the weight average molecular weight of the block A2, is usually, in the range of 5000 ~ 200,000, and preferably it is in the range of 10,000 ~ 150,000, and then more preferably, it is in the range of 15,000 ~ 100,000. And in the case when that weight average molecular

weight is less than 5,000, the compatibility properties relative to the olefin type polymer material that has ethylene as its main component, are decreased and that is why it is not a preferred option. And on the other hand, in the case when that weight average molecular weight exceeds 200,000, the flowability properties are poor, and the processing properties are deteriorated, and because of that it is not a preferred option. Regarding the proportion of the block A2 in the component (ha), as it has been described here above, it varies depending on the target application. In the case where the block A2 is a component that is essential to maintain the compatibility properties relative to the olefin type polymer material that has ethylene as its main component (case 1), it is contained in the range of 2 ~ 98 weight %, preferably, in the range of 10 ~ 80 weight %, and then more preferably, in the range of 15 ~ 70 weight %, in the component (ha). In this case, when the contained amount is less than 2 weight %, or when it exceeds 98 weight %, the performance as a component (ha) compatibilizing agent, is deteriorated.

[0016]

On the other hand, in the case when the compatibility properties relative to the olefin type polymer material are supported by the block B (case 2), it is also a good option even if there is no block A2 contained in the component (ha). However, in the case of a component (ha0, that is formed only from the block A and a high vinyl content block B, even if the above block A and B ratio is present, the surface has sticky properties, and it is a case when it has adhesion properties. Because of that, it is easy to generate handling problems. By bonding of appropriate amount of the block A2, the adhesion properties are decreased, and the handling properties are improved. Consequently, in the case of Case 2, the proportion of the block A2 in the component (ha) is in the range of 0 ~ 98 weight %, and preferably, it is in the range of 1 ~ 50 weight %, and then more preferably, it is in the range of 3 ~ 30 weight %. And in the case when that proportion exceeds 98 weight %, it becomes a material that has poor capability as a component (ha) compatibilizing agent.

[0017]

According to the present invention, the hydrogenation ratio of the component (ha) is at least 90 % or higher, and preferably, it is at least 94 % or higher, and then even more preferably, it is at least 96 %, or higher.

In the case when the hydrogenation ratio is less than 90 %, because of the residual unsaturated double bond, the decrease of the thermal resistance properties and the weather resistance properties, is significant.

The component (ha), used according to the present invention can be obtained according to the method that has been disclosed in the description reported in the Japanese Patent Application Laid Open Number Hei-Sei 2-133406.

[0018]

According to the composition of the present invention, the olefin type polymer material (i), is usually contained in an amount that is in the range of 10 ~ 99.4 weight %, and preferably, it is in the range of 60 ~ 99.4 weight %, and the crosslinked styrene type polymer material (ro), is usually contained in amount in the range of 0.5 ~ 70 weight %, and preferably, it is in the range of 0.5 ~ 30 weight %. The hydrogenated block copolymer material (ha) is usually contained in an amount that is in the range of 0.1 ~ 20 weight %, and preferably, it is in the range of 0.1 ~ 10 weight %.

[0019]

The thermoplastic resin composition material according to the present invention has the above described components (i) ~ (ha), as its main components, however, besides those, it is also possible to appropriately compound the following materials: 2, 6 – di – t- butyl – 4 – methyl phenol, 2 – (1-methylcyclohexyl) – 4, 6 –dimethyl phenol, 1, 6 hexane diol – bis [3 – (3, 5 – di – t- butyl – 4 – hydroxyphenyl) propionate], pentaerithrityl – tetrakis [3- (3, 5 – di – t – butyl – 4 – hydroxyphenyl) propionate] etc., hindered phenol type anti-oxidation agents, pentaerithritol tetrakis (3-lauryl thiopropionate), dilauryl 3, 3' – thiodipropionate, etc., thioether type anti-oxidation agents, tris nonyl phenyl phosphate, distearyl pentaerithritol disphite etc., phosphorus type anti-oxidation agents; stearoamide propyl dimethyl - β - hydroxy ethylammonium nitrate, etc., anti-electrostatic agents; 4-acetoxy – 2, 2 , 6 – tetramethyl piperidino, 4 – stearoyloxy – 2, 2, 6, 6 – ttetramethylpiperidine, etc., weather resistance agents; p – t – butyl phenyl salicilate, 2, 2 '- dihydroxy – 4 – methoxybenzophenone, etc., ultra-violet rays absorbing agents; paraffin wax, polyethylene wax, high

homologous order aliphatic acids, or their metal salts, etc., lubricating agents; titanium oxide, carbon black, etc., coloring agents; glass fibers, carbon fibers, metal fibers, aramide fibers, glass beads, asbestos, mica, calcium carbonate, potassium titanate whiskers, talcum, barium sulfate, glass flakes, fluorine containing resin materials, etc., filler agents; or other rubber type polymer materials, thermoplastic type resin materials, etc. Also, depending on the requirements, it is possible to appropriately compound 1 – menthol, citrus type oils, etc., aromatic agents. The composition material according to the present invention can be prepared by melting and mixing by using an extruder, a kneader, a Bumbarry mixer etc.. Regarding the manufacturing of the composition material according to the present invention, it is a good option if each of the components are mixed as a bundle, at once, and it is also a good option if any of the components are mixed in advance and after that the remaining components are added. The most appropriate manufacturing device is a uniaxial or biaxial extruder, and by it is possible to continually mix at a good efficiency, and pelletize. By using the obtained pellets, extrusion and molding is conducted and it is possible to process the material into molded (formed) products. As the molded products that are obtained by using the composition material according to the present invention and extruding and molding, it is possible to have sheet materials, film materials, tube materials etc., and these can be used in different applications.

[0020]

[Practical Examples]

Here below, practical implementation examples will be presented and the present invention will be then explained in more details, however the present invention is by no means limited by those practical examples. Moreover, the parts and %, that are references within the description of the practical implementation examples are based on weight, except when state otherwise. Also, the different measurements that are found in the practical examples have been conducted according to the described here below methods.

(1) Content of the bonded vinyl aromatic compound

This content was measured by Infra-Red Spectroscopy, based on the absorption of the phenyl radical at 679 nm – 1.

(2) Content of the conjugated diene vinyl bond

This was obtained by using the Infra-Red Spectroscopy method and calculating according to the Hampton method.

(3) Hydrogenation ratio

This was calculated from the 1H-NMR spectrum, obtained at 10 MHz by using ethylene tetrachloride as the solvent medium.

(4) Weight average molecular weight

This was obtained by calculation as polystyrene, by using Gel Permeation Chromatography (GPC) method, at a temperature of 135oC, and employing trichlorobenzene as the solvent medium.

(5) Density

The density was measured according to the described in JIS K-7112.

(6) Melt Flow Rate (MFR)

This was measured according to the described in the JIS K 7210, at a temperature of 230oC, load of 2.16 kg.

7 Isod Impact Strength

This was measured according to the procedures described in the JIS K 7110.

(7) Tensile properties

These were measured according to the procedures describe din the JIS K 7113.

[0021]

Manufacturing of the component (ro)

98 parts of styrene, 2 parts of methacrylic acid, 10 parts of t-dodecyl mercaptane, were added into 200 parts of water where 0.5 parts of sodium lauryl sulfate and 1.0 parts of potassium persulfate have been dissolved, and while stirring polymerization was conducted at a temperature of 70oC for a period of 8 hours, and by that polymer particles, were obtained. These polymer particles, had an average particle diameter of 0.22 microns, their toluene insoluble part was 3 %, and their number average molecular weight determined by GPC was 4,100, and the ratio of the weight average molecular weight and the number average molecular weight, Mw/Mn = 2.4. After that, these polymer particles were used as the seed polymer and 10 parts, as solid phase part, of these polymer particles,, 0.1 part of polyoxyethylene nonyl phenyl ether, 0.3 parts of sodium lauryl sulfate, and 0.5 parts of potassium persulfate, were dispersed in 900 parts of water. To that a mixture of 80 parts of methyl methacrylate, 10 parts of divinyl benzene (calculated as pure product), 10 parts of styrene, was added, and this was stirred at a temperature of 30oC for a period of 1 hour, and when that was done, the above described material was almost completely adsorbed on the seed polymer particles. This was polymerized in the state as it is for a period of 5 hours at a temperature of 70oC, and when that was done, a pH 3.0 water dispersion of hollow crosslinked polymer particles (here below, called hollow particles (ro)) was obtained at a polymerization yield of 98 %.

[0022]

Manufacturing of the (ha) component (Manufacturing of ha – 1 ~ 5)

In a autoclave with a total capacity of 5 liters, 2.5 kg of cyclohexane, 500 grams of 1, 3 – butane diene, 0.4 grams of n-butyl lithium, were added, and at a temperature of 50oC, the polymerization conversion ratio became 18 %. And after that, 9.8 grams of tetrahydrofuran, were added and the temperature was increased, and a polymerization was conducted until the polymerization conversion coefficient became 100 %. After that, 90 grams of styrene were added, and the polymerization was completed. After the completion of the polymerization, the reaction solution was adjusted to a temperature of 70oC, and 0.8 grams of n-butyl lithium, 0.8 grams of 2, 6 – di – t – butyl – p – cresol, and 0.25 grams of bis (cyclopentadienyl) titanium dichloride, and 1 gram of diethyl aluminum chloride, were added, and this was reacted for a period of 1 hour at a hydrogen pressure of 10 kg/cm2. This reaction solution was mixed in a large amount of methyl alcohol, and the separated solid

phase material was extracted, and dried and by that the hydrogenated block copolymer material ro – 1, was obtained. The hydrogenation coefficient of the obtained hydrogenated block copolymer material ro –1, was 99 %, and the first phase 1, 2 – vinyl bond content was 12 %, and the second phase 1, 2 – vinyl bond content was 40 %. Also, the type of the monomer material, the amount of the monomer material, the amount of the catalyst material, the polymerization temperature, the polymerization time, etc., were varied so that the hydrogenated block copolymer materials shown according to Table 1, were obtained, and these were produced by using the procedures for the hydrogenated block copolymer material ha – 1, and by that the hydrogenated block copolymer materials ha – 2 ~ 5, were prepared.

Structure 1: block A1 – block B – block A2

Structure 2: block A1 – block B

[0023]

Practical Examples 1 ~ 7

By following the compositions presented according to table 1, the resin mixtures were prepared, and by using a biaxial extruder PCM 45, manufactured by Chibai Tetsuko Company, these were palletized. By using the obtained pellets, and by using the injection molding method, test pieces were obtained. The results are presented in Table 2.

[0024]

Reference Examples 1 ~ 7

By following the compositions presented according to table 3, the resin mixtures were prepared, and by using a biaxial extruder PCM 45, manufactured by Chibai Tetsuko Company, these were palletized. By using the obtained pellets, and by using the injection molding method, test pieces were obtained. The results are presented in Table 3. Moreover, the resin types used according to the presented in table 3, are shown here below.

Low density polyethylene: manufactured by Tosoh Company, Petrocene 190

Polypropylene: MA-2A, manufactured by Mitsubishi Petrol Company

G1650: SEBS, hydrogenated block copolymer material obtained by the hydrogenation of styrene – butadiene-styrene block copolymer material; manufactured by Shell Company, its microstructure is such that it contains approximately 40 weight % of butadiene block, which has 1, 2 – vinyl bond.

A1100: Modipar 1100 (grafted copolymer material where polystyrene has been grafted in a polyethylene chain), manufactured by Nippon Petrol Company

[0025]

[Table 1]

1

		ハ−1	ハ−2	ハ−3	ハ−4	ハ−5
3	(ハ) 成分の構造	構造1	構造1	構造1	構造1	構造2
4	(ハ) 成分のミクロ構造				2	
5	ブロックA1 (重量%)	15	30	20	30	40
6	ブロックA2の1，2−ビニル結合含量 (%)	12	12	13	12	-
7	ブロックA2 (重量%)	15	15	20	5	-
8	ブロックBの1，2−ビニル結合含量 (%)	40	42	43	85	85
9	ブロックB量 (重量%)	70	55	60	65	60
10	(ハ) 成分の物性					
11	水添率 (%)	99	99	98.5	99.5	99
12	MFR (g/10分)	0.1	0.1	0.01	0.5	1.0
13	重量平均分子量 (×10⁴)	10	10	22	15	20

Headings in the table:

1. ha #…, 2. Structure 1 or 2, 3. structure of the component (ha), 4. microstructure of the component (ha), 5. block A1 (weight %), 6. content of the 1,2 – vinyl bond of the block A2 (%), 7. block A2 (weight %), 8. content of the 1, 2 – vinyl bond of the block B (%), 9. amount of the block B (weight %), 10. properties of the component (ha), 11. hydrogenation coefficient, 12. MFR 9g/10 minutes)< 13. weight average molecular weight (x 10 4 power).

[0026]

Table 2

	実施例 /						
	1	2	3	4	5	6	7
2 (イ) 成分 3 種類 4 (部)	5 低密度ポリエチレン (50)	5 低密度ポリエチレン (30)	5 低密度ポリエチレン (70)	5 低密度ポリエチレン (50)	5 低密度ポリエチレン (50)	MA−2A (50)	MA−2A (50)
6 (ロ) 成分 7 種類 8 (部)	9 中空粒子(ロ) (50)	9 中空粒子(ロ) (70)	9 中空粒子(ロ) (30)	9 中空粒子(ロ) (50)	9 中空粒子(ロ) (50)	9 中空粒子(ロ) (50)	9 中空粒子(ロ) (50)
10 (ハ) 成分 11 種類 12 (部)	13 ハ-1 5	ハ-1 5	ハ-1 5	ハ-2 5	ハ-3 5	ハ-4 5	ハ-5 5
物性 14							
比重 15	0.83	0.78	0.87	0.87	0.84	0.84	0.84
MFR (g/10分) 16	23	38	18	27	16	28	40
アイゾット 17 衝撃強度 18 (kgcm/cm)	15	7	30	18	22	7	8
引張強度 19 (kg・cm2)	160	200	120	170	160	170	180
引張伸び 20 (%)	40	30	130	40	50	60	50

Headings in Table 2:

1. Practical Example number…, 2. (i) component, 3. type, 4. (parts), 5. low density polyethylene, 6. (ro) component, 7. type, 8. (parts), 9. hollow particles (ro), 10. (ha) component, 11. type, 12. (parts), 13. ha-…number, 14. Properties, 15. density, 16. MFR (g/10 minutes), 17. Isod Impact Strength (kgcm/cm), 19. tensile strength (kg.cm2), 20. tensile elongation (%).

[0027]

[Table 3]

	比較例 1				
	1	2	3	4	5
2 (イ) 成分	4				
オレフィン系重合体 3 種類 (部)	低密度ポリエチレン (50)	← (50)	← (50)	MA-2A (50)	← (50)
5 (ロ) 成分					
架橋スチレン系重合体 6 種類 (部)	(50)	← (50)	← (50)	← (50)	← (50)
7 (ヘ) 成分					
8 種類	-	G-1650	A-1100	-	G-1650
9 部	-	5	5	-	5
10 物性					
11 比重	0.84	0.84	0.84	0.84	0.84
12 MFR (g/10分)	25	6	20	40	20
13 アイゾット衝撃強度 (kg・cm/cm)	2.0	3.0	2.5	2.0	3.5
14 引張強度(kg/cm ^{2})	160	160	150	180	160
15 引張伸び (%)	20	25	20	10	15

Headings in Table 3:

1. Reference Examples, 2. (i) component, 3. Type and parts of the olefin type polymer material, 4. low density polyethylene, 5. (ro) component, 6. crosslinked styrene type polymer material type (parts), 7. (ha) component, 8. type, 9. parts, 10. Properties, 11. density, 12. MFR (g/10 minutes), 13. Isod Impact Strength (kgcm/cm), 194. tensile strength (kg.cm2), 15. tensile elongation (%).

[0028]

[Results From the Present Invention]

The component (ha) used according to the present invention, when used in a small amount, compatibilizes the blend formed from the olefin type polymer material and the crosslinked styrene type polymer material, and it is possible to suggest a polymer material with excellent properties. Because of that, in the case of the thermoplastic resin composition material according to the present invention, the resolution of the drawbacks of the olefin type polymer material and the crosslinked styrene type polymer material is helped, and it is a material that has light weight and has excellent impact resistance properties and excellent mechanical strength properties, and it is a material that can be used in a wide sphere of applications.

Patent Assignee: Nippon Gosei Company